❊ *Second Place Winner in 1995 Roon Awards Competition* ❊

Film Formation Mechanism of Two-Component Waterborne Polyurethane Coatings

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INTRODUCTION

Two-component (2K) waterborne polyurethane coatings are a relatively new technology which has been demonstrated in automotive, aerospace, industrial maintenance, wood, and plastic coating applications.[1-6] They consist of a water dispersible, multi-functional isocyanate which is mixed with a dispersion of hydroxy-functional polymer. The popularity and importance of these coatings is growing significantly due to their potential for providing excellent properties, equivalent to those of their solvent-borne counterparts, combined with a low concentration of volatile organic compounds (VOCs). Current waterborne formulations have VOCs of less than 250 grams per liter of paint and this evolving technology has the potential for eliminating VOCs entirely.

Although researchers have been successful in developing these coatings into practical systems, one important aspect that is not well understood is their film formation mechanism. This is due to their relatively recent development, as well as the complexity of their drying/curing process. As with all coatings, proper film formation is essential for optimum coating performance. Film formation of 2K waterborne polyurethanes is especially critical due to their use in heavy duty applications where long-term performance (e.g., adhesion, durability, substrate protection) is paramount. Their film formation process is unusually complex and consists of a dynamic series of events which are interrelated. The order of and extent to which these events occur has a major impact on the quality and performance of the applied coating. The film formation process includes the traditional difficulties of water-based systems, namely evaporation of water and organic volatiles with concomitant coalescence of polymer particles. It is complicated further by the need for thorough coalescence of dissimilar species (polyisocyanate and polyol) and competing reactions between hydroxyl groups and water with the isocyanate (*Figure* 1). Furthermore, the reaction of isocyanate with water ultimately produces carbon dioxide which must leave the system in such a way as to avoid film defects. Although these critical issues have been recognized, until now no detailed film formation mechanism for these systems has been proposed and substantiated.

Two-component (2K) waterborne polyurethane coatings are a new technology which has been demonstrated in a number of heavy duty applications. They exhibit performance properties equivalent to 2K solvent-borne polyurethanes, with the advantage of reduced volatile organic compounds (VOCs). Although the use of these systems has been demonstrated successfully, the details of their film formation mechanism have not been established.

The objective of this work was to propose and confirm the film formation mechanism of these systems. A dynamic series of interrelated events which occur during the process was identified using a number of analytical techniques to study two isocyanate/hydroxyl functional dispersion systems. The mechanism is presented in terms of an "event timeline" that chronicles the critical events which occur prior to and after application of the coating.

Film property development after application also was evaluated and these results were analyzed in terms of the proposed film formation mechanism.

The objective of this work was to propose and confirm the film formation mechanism of 2K waterborne polyurethane coatings. The approach was to isolate each of the events which occur along the timeline of this process, identify the critical issues influencing these events, and determine the extent to which film formation and coating properties are affected by these events. With a better understanding of these factors, the chemistry and formulation of these systems can be adapted to increase the latitude of their applications while minimizing the potential for defects caused by poor film formation. In this paper we present the following:

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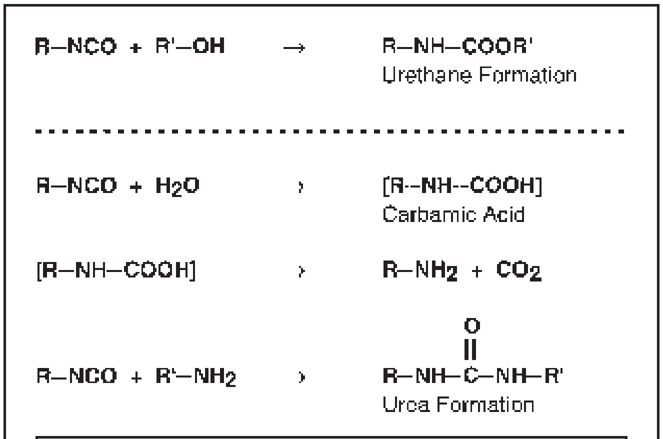

Figure 1—Reactions of isocyanate with hydroxyl and water.

(1) A brief review of film formation mechanisms, concentrating mainly on those issues pertinent to 2K waterborne polyurethanes.

(2) A proposed mechanism for these systems which describes the timeline of events and their respective interactions.

(3) A description of the experimental details.

(4) Empirical results which confirm the proposed mechanism and identify the critical issues affecting coating properties.

BACKGROUND ON FILM FORMATION

As mentioned previously, proper film formation is critical to coating performance and much research has been performed to determine film formation mechanisms for various types of coatings. In general terms, it is convenient to classify these as:

(1) Thermoplastic polymers from solution.
(2) Thermoplastic polymers from dispersion.
(3) Thermosetting polymers from solution.

Clearly, film formation of thermosetting polymers from dispersion and, more specifically, that of 2K waterborne polyurethane coatings is not covered under these traditional categories. It would seem, however, that some principles associated with film formation of thermoplastics from dispersion and thermosetting polymers from solution would be related to those of 2K waterborne polyurethanes. Certainly the requirements of particle coalescence (associated with dispersions of thermoplastics) and crosslinking reactions (associated with thermoset systems) must exist with 2K waterborne polyurethanes. A more detailed look at the mechanisms of the former systems will provide insight concerning that of the latter.

Traditional waterborne coatings are prepared from an aqueous dispersion of polymer particles, commonly referred to as a latex. *Figure* 2 is a schematic that depicts their basic film formation process. Upon application of the latex, water and other volatile components begin to evaporate, forcing the polymer particles closer together. As this evaporation process continues, the concentration of polymer particles increases until eventually the particles come into contact. At this point they have formed a close-packed arrangement with volatiles in the interstitial regions. As the remaining volatiles evaporate from within the polymer particles and the interstitial regions, forces begin to compress and coalesce the particles. Numerous models and mechanisms have been proposed on the origin and extent of these forces[7-11] but all agree that complete film formation of these systems requires diffusion of polymer molecules across particle boundaries. As this occurs, individual particles cease to exist. Cohesive strength of the film is enhanced significantly by increased chain entanglements and secondary bonding. The end result is the formation of a solid, cohesive film on the substrate.

A critical factor in this film formation process is the diffusion of polymer molecules required for coalescence. This is associated with large-scale motion of molecular chains, such that polymers at temperatures above their glass transition temperature, (T_g) will form films more easily than those below their T_g. Unfortunately, polymers with lower T_g normally produce coatings with lower strength, durability, abrasion, and chemical resistance. To overcome these performance deficiencies, higher T_g and higher molecular weight polymers are used. In order to properly film form, such dispersions require either additional solvent to swell the polymer particles (thereby reducing T_g), or higher drying temperature, which increases the mobility of the polymer chains. Of course these modifications cause higher VOCs or baking requirements which are undesirable for many applications.

Film formation of thermosetting polymers from solution occurs via a completely different mechanism from that described previously. In this case, the system is a solution of reactive species in organic solvents. The solvents are selected to keep the coating in a liquid state until application, at which time they begin to evaporate. The reaction, which is designed to build molecular weight and crosslinking of the polymer, normally can proceed prior to and/or after application of the coating. In the case of two-component coatings (e.g., 2K epoxies and polyurethanes), the reaction kinetics occur quickly enough that the reactants must be mixed just prior to application or else the systems will gel prematurely. Two-component polyurethanes normally are formed from the reaction of a multi-functional isocyanate with a hydroxy-

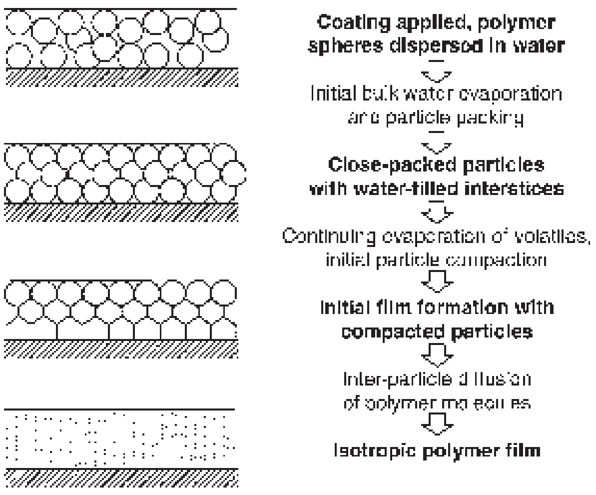

Figure 2—Latex film formation mechanism.

functional polyester or acrylic. In this case, the kinetics normally follow a second order relationship.[12] (Note: The gel time of these 2K solvent-borne polyurethane coatings ranges from several minutes up to eight hours depending on the specific reactants, catalyst(s), and application/cure temperature.)

A critical issue associated with this mechanism is the relative rate of solvent evaporation versus that of the curing reaction. Rapid curing reaction and the associated molecular weight increase can cause a number of potential problems. Solvents may become trapped and eventually form small blisters or "solvent pops" within the film. In addition, if molecular weight builds too quickly during the early stages of curing, diffusion of reactive groups can become hindered. This prevents complete reaction and leaves unreacted lower molecular weight species within the film. These unreacted molecules usually have detrimental effects on mechanical and chemical resistance properties. Finally, quick reactions will shorten pot life and may cause immobility of the molecular system. This latter effect may result in internal stresses within the coating which are potential sites for mechanical failure. On the other hand, slow reactions can cause slow drying and property development which also is undesirable.

From the description of 2K waterborne polyurethane coatings provided in the Introduction Section, one would imagine that some facets of their film formation mechanism would be related to a combination of those described. It would appear that the following steps must take place in some overlapping order:

- Evaporation of volatiles;
- Coalescence of polyol and polyisocyanate particles; and
- Reaction between polyol and polyisocyanate.

This process is complicated by the fact that when the components of the coating are combined the reactive species are not immediately in the same phase within the dispersion but ultimately must be so to react. It is further complicated by the competing reactions of isocyanate with both hydroxyl groups and water (*Figure* 1). While the former reaction yields the preferred polyurethane, the latter reaction produces urea and CO_2. The CO_2 must leave the coating before the completion of film formation to avoid defects within the bulk or the surface of the cured coating.

Some researchers have provided limited evidence as to the order and extent of events during film formation of these systems. It has been suggested that as the two components are mixed, the polyol dispersion emulsifies the isocyanate by encapsulating it.[3,4,6,13] Kubitza[13] reported polyisocyanate particle size of 0.1 to 0.5 microns (depending on agitation severity) shortly after mixing with a hydroxy-functional acrylic dispersion. After one hour, particle diameters of up to 10 microns were measured. Jacobs and Yu[4] utilized a hydroxy-functional polyurethane dispersion with a particle size of less than 25 nm but reported the dispersed polyisocyanate particle size was approximately two microns. In fact, scanning electron micrographs of applied polyisocyanate from a five percent aqueous dispersion illustrated isolated particles 1 to 10 microns in diameter. Bock and Petzoldt[6] also reported that they observed an isocyanate-enriched phase with larger particles than the initial dispersion.

Mixing of the polyisocyanate and polyol dispersion prior to application will initiate the isocyanate-hydroxyl and isocyanate-water reactions. If coalescence of polyisocyanate and hydroxy-functional particles occurs at this time, it will facilitate the preferred isocyanate-hydroxyl reaction. This effect is enhanced even further if the polyol "encapsulates" the polyisocyanate. Hare[14] has stated that this encapsulation does occur and the reaction initiates at hydrophilic centers at the polyisocyanate-polyol interface. The reaction of typical polyisocyanates with hydroxyl appears to be faster than that with water.[4,15,16] However, some reaction with water is inevitable. Bock[6] has reported detection of CO_2 approximately 30 min after mixing. To ensure complete reaction of hydroxyls, it has become common to use excess polyisocyanates at NCO/OH ratios of 1.5 to 3.

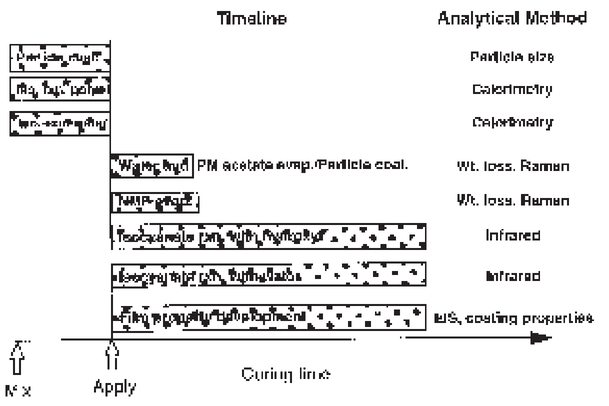

Figure 3—Proposed film formation mechanism "event timeline" for 2K waterborne polyurethane coatings.

The coating must be applied before the curing reaction(s) proceed to any substantial extent. Otherwise, molecular weight and crosslinking would occur to such an extent that particle coalescence after application would be difficult due to diffusion limitations. Upon application of the coating, volatiles (water and solvents) begin to evaporate. It has been stated that most of the water has evaporated in 20 to 60 min after application.[4,14] This forces the particles together, allowing for more thorough diffusion and reaction. Ultimately, a crosslinked polymer coating is formed. Jacobs and Yu[4] reported that maximum levels of solvent resistance, impact resistance, and hardness were reached in two days, and ultimate tensile strength was fully developed in four to five days. They related these results to dynamic mechanical analysis results which showed that storage modulus stabilization occurred after two days but it took three days for stabilization of tan δ curves. Kubitza[13] found T_g values from DSC data increased until day 12.

PROPOSED FILM FORMATION MECHANISM FOR 2K WATERBORNE POLYURETHANE COATINGS

The mechanism is presented in terms of an "event timeline" that identifies the following interrelated processes that occur during film formation: particle coalescence, reactions of isocyanate with hydroxyl groups and water, water evaporation, and solvent evaporation. These are schematically depicted in *Figure* 3. All these events interact to establish the film chem-

Table 1—Materials and Suppliers

Product	Description	Manufacturer
Hybridur® 710EXP (ACPU-1)	Hydroxy-functional acrylic-polyurethane	Air Products and Chemicals, Inc.
Bayhydrol® XP-7044 (PUD-1)	Hydroxy-functional polyurethane	Miles, Inc. (now Bayer)
Bayhydur® XP-7063	HDI based polyisocyanate	Miles, Inc. (now Bayer)
Dabco® T1402	Dibutyltin Bis(1-thioglycerol)	Air Products and Chemicals, Inc.
BYK® 345	Polyether modified polydimethylsiloxane	BYK-Chemie, Inc.

istry and development of mechanical integrity during cure. The event timeline starts after mixture of the two components, at which point particle coalescence and isocyanate chemistry are the key processes that affect the coating system. After coating application, these continue to affect the system, however, water and solvent evaporation now become key processes as well.

To verify this mechanism and generate an understanding of the time frame in which these events dominate, a number of analytical characterization tools were utilized with two isocyanate/hydroxy-functional dispersion systems (as listed in *Figure* 3 and described in the Experimental Section). Particle coalescence was measured by particle size as a function of induction time (i.e., the time elapsed after mixing the two reactive components). The reaction chemistry and rates during this time were monitored using isothermal calorimetry which was correlated with viscosity effects. After application of the coating, particle packing factor calculations coupled with weight loss data were used to study the initial phase of coalescence as water evaporated and particle close-packing was achieved. Water and solvent evaporation were monitored by weight loss studies and infrared (IR) spectroscopy. Film formation was also studied using electrochemical impedance spectroscopy (EIS) and Raman spectroscopy. Isocyanate reaction chemistry of applied films was monitored by infrared, and EIS studies. The surface chemistry after cure was examined using X-ray photoelectron spectroscopy (XPS).

In addition to the analytical approach described previously, the development of film properties was characterized. This was completed by performing standard chemical and mechanical evaluation techniques on coatings as a function of time after application. EIS was also performed as part of this evaluation.

Table 2—Properties of Dispersions and Isocyanate Used

Property	PUD-1	ACPU-1	Isocyanate
Solids, wt%	40	43	100
Water, wt%	47	50	0
N-methylpyrrolidinone (NMP), wt%	11	7	0
Equivalent wt.	2200	1810	243
Density, g/ml	1.06	1.04	1.16

Table 3—Typical Hydroxy-Functional Acrylic-Polyurethane Based Formulation Evaluated

	Percent by Weight
ACPU-1	70.27
BYK 345	0.28
Dabco T1402	0.02
XP-7063	19.20
PM acetate	10.23

EXPERIMENTAL

Materials and Coating Preparation

The materials used in this study and their manufacturer are listed in *Table* 1. These systems are representative of available 2K waterborne polyurethane technology. Two hydroxy-functional dispersions were utilized, a polyurethane (PUD-1) and an acrylic-polyurethane hybrid (ACPU-1). These dispersions were crosslinked with a hexamethylene diisocyanate (HDI) trimer which was modified to improve water dispersibility. *Table* 2 lists properties of these materials. Further material descriptions are provided in references (17) and (18).

Coatings were prepared by adding surfactant and catalyst to the hydroxy-functional dispersion while mixing under mild agitation. The surfactant was added at a concentration of 0.4% by weight of the dispersion. Catalyst concentration was 0.04% by weight based on total polymer solids of the final coating. A 65% solution of the isocyanate in propylene glycol methyl ether (PM) acetate was prepared. When combined with the aqueous dispersions, a coating VOC (minus water) of approximately 250 grams per liter was formed. The admixed coating was prepared prior to application by adding the isocyanate solution to the dispersion while under mild agitation. The components were combined to obtain an NCO/OH ratio of 2.0. *Table* 3 provides an example of the ACPU-1 formulation evaluated. The standard induction time prior to application of the admixed coating was 15 min; however, the effects of induction time on heat of reaction and dispersion particle size were studied. Unless otherwise specified, the coatings were applied to a dry film thickness of 50±5 microns (2±0.2 mils) using conventional air spray. Coatings were applied to cold rolled 1020 steel with a zinc phosphate treatment (Bonderite® 952) and a chromate sealer (Parcoolene® 60). Unless otherwise noted, the coating drying and storage conditions were 21°C, 50% relative humidity.

Equipment and Procedures

Table 4 lists the ASTM methods used to evaluate admixed and applied coating properties. Weight loss of applied coatings after application was obtained by applying a film with a 152 micron (6 mil) drawdown bar and weighing the sample at specified time intervals after application. The property development assessment was done by preparing the specimens described earlier and performing specified tests at predetermined times after application.

Table 4—Procedures Used to Evaluate Admixed and Applied Coatings

Property	ASTM Method
Viscosity (Zahn 2)	D4212
Adhesion	
Tape adhesion	D3359A
Scrape adhesion	D2197A
Persoz hardness	D4366
Solvent resistance	D4752

Particle size distributions of dispersions were obtained using capillary hydrodynamic fractionation (CHDF).[19] Samples were prepared by mixing the isocyanate solution (XP-7063/PM acetate) into the desired hydroxy-functional dispersion to obtain an NCO/OH ratio of 2.0. After combining the two materials, the dispersions were shaken vigorously for 1-2 min. A sample of XP-7063/PM acetate solution was also mixed into water. Particle size measurements were periodically obtained for these samples over their pot life. Just prior to particle size analysis, a sample of each dispersion was diluted to one percent solids using distilled water and injected into the CHDF. The particles flow within a capillary tube. The laminar flow profile within the tube causes the particles to separate according to size with the larger particles leading the flow and exiting the capillary first, followed by smaller particles. The particles are detected via turbidity using a UV detector. The chromatograms were deconvoluted to generate number and weight average particle size diameters and distributions.

Heat flow profiles for the reaction of isocyanate with hydroxy-functional dispersion and water were obtained with a Setaram C80D (differential heat flux) calorimeter. Identical test cells are placed into sample and reference chambers within the temperature control block. Thermopiles are used to monitor the heat flow into or out of each chamber. The difference between the sample and reference signals is used to eliminate heat flux associated with temperature control of the calorimeter. For the present work, the calorimeter was used isothermally at 21°C. Prior to mixing, the isocyanate solution and aqueous dispersion components were placed into the lower and upper chambers of the stainless steel membrane mixing cell, respectively. The chambers were separated by a Teflon membrane. The upper chamber of the reference cell was filled with the same amount of dispersion as in the sample cell, but the lower chamber was left empty. After insertion of the cells into the calorimeter, and equilibration to a stable heat flux baseline, the membranes of the sample and reference cells were punctured simultaneously, and the cells were mixed using manual impellers for one minute. Following that process, the cells were not disturbed as the heat flux was monitored over a 24-hr period.

IR spectroscopy was done using an attenuated total reflectance (ATR) system which allowed the coating to be measured during cure.[20] A CIC Photonics Fresnel ATR held the crystal horizontally inside the IR (Nicolet 510 interferometer) sample compartment. A 45° incident angle AMTIR-1 crystal (2 cm diameter sampling area) was used. A film was spread onto the crystal with a 127 micron (5 mil) draw-down bar. The infrared spectrum was obtained by co-adding 64 scans at 4.0 cm^{-1} resolution, and spectra were obtained and saved at 15-min intervals for 24 hr and then daily for three weeks.

Electrochemical impedance spectroscopy (EIS) was performed using a commercial coatings cell (EG&G Instruments) with a 1 cm diameter gasket defining the working electrode in a three electrode cell. Measurements were controlled by a commercial software package (EG&G 398) with a potentiostat (EG&G 273A) and lock-in amplifier (EG&G 5210) at individual frequencies for 5 Hz to 100 kHz. Low frequency data were obtained in a multi-sine wave experiment. The data were combined into one EIS spectrum for analysis. Modeling was done using Equivcrt,[21] and a simple coating model (pore resistance and coating capacitance) was used to evaluate the coatings.

EIS was used in two ways in this work. To probe effects of water evaporation and film formation over time, coatings were drawn onto the substrate and pieces were cut with tin shears at specified time intervals and analyzed. EIS spectra were obtained after 15 min of equilibration in 3% NaCl solution to minimize the effect of contact with electrolyte on the curing film. A comparison with fully cured coatings was made in EIS experiments done after 15 min and after 24 hr exposure to NaCl solution. These studies were done at three locations on the coating.

The surface composition of cured coatings was determined with XPS using a PHI (Physical Electronics) 5000LS surface spectrometer, equipped with a hemispherical analyzer (SCA), an Omni Focus III lens system, and a multi-channel detector (MCD). Maximum sampling depth was about 10 nm. High resolution multiplex spectra were collected, for each elemental species detected in the survey scan, at 23.50 eV Pass Energy, 0.100 eV per step, and 100 ms per step. The high resolution regions were used to calculate the surface composition by measuring the area under each peak envelope and

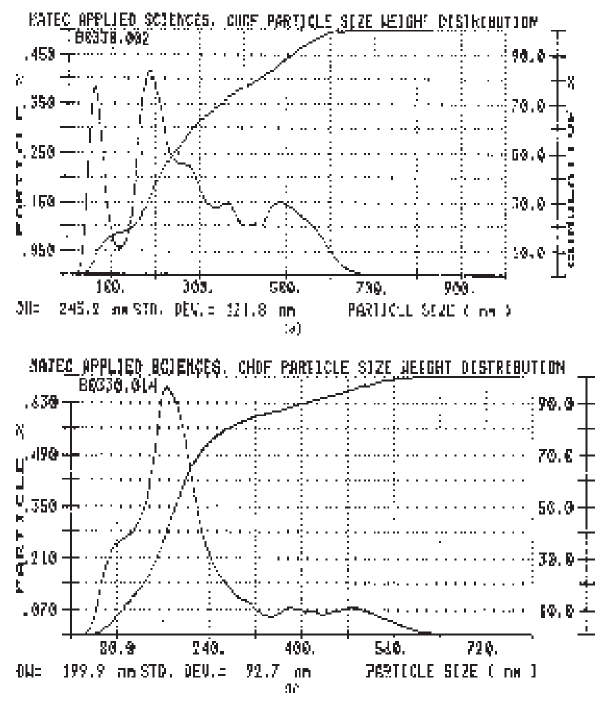

Figure 4—Particle size weight distributions of the isocyanate/water dispersion after induction times of (a) 15 min and (b) 4.2 hr.

Table 5—Particle Size (nm) of Dispersions

Induction Time	Isocyanate in water			Isocyanate in ACPU-1			Isocyanate in PUD-1		
(hr)	D_n	D_w	D_w/D_n	D_n	D_w	D_w/D_n	D_n	D_w	D_w/D_n
0.0	76	245	3.2	66	206	3.1	62	323	5.2
0.5	—	—	—	70	213	3.0	56	310	5.5
1.0	79	263	3.3	—	—	—	—	—	—
1.5	—	—	—	—	—	—	—	—	—
2.0	82	245	3.0	74	142	1.9	62	276	4.5
3.25	—	—	—	79	172	2.2	58	271	4.7
4.25	102	200	2.0	79	140	1.8	62	252	4.1
5.5	114	223	2.0	81	148	1.8	59	261	4.4
7.0	96	210	2.2	66	75	1.1	—	—	—

applying area sensitivity factors (ASF) in the analysis software.

RESULTS AND DISCUSSION

Results from the range of analytical tests are described in the context of the timeline of events which we propose occurs during the entire film formation sequence as outlined in *Figure* 3. Film property development after application was evaluated using EIS and other standard coating characterization methods. These results were analyzed in terms of the proposed film formation mechanism.

Particle Coalescence in the Admixed State

After mixing but prior to application (referred to as the induction time), the events which may potentially occur relative to film formation are coalescence of isocyanate particles with the hydroxy-functional dispersion particles, and reactions of the isocyanate with both hydroxyl groups and water (*Figure* 1). Particle coalescence during this stage of film formation was analyzed using in-situ particle size measurements. Prior to mixing with the isocyanate, ACPU-1 had a number average particle size (Dn) of 66 nm, a weight average particle size (Dw) of 75 nm, and Dw/Dn = 1.1. The particle size distribution curves for ACPU-1 had a classic Gaussian shape. PUD-1 has a particle size of ~25 nm.[4] Particle size data over the induction time are listed in *Table* 5.

The dispersion of isocyanate in water had an initial average particle size of Dw = 245 nm and Dn = 76 nm. Dw decreased slightly over the seven-hour induction time down to 210 nm. Similar studies were obtained with both mild and vigorous agitation. In addition, the graph of particle size weight distribution went from the initial multi-peak distribution to a single peak distribution at 4.25 hr (*Figure* 4). The graphs suggest that smaller particles (D ~60 nm) are growing in size but large particles (D ~200 nm) do not seem to be changing. Particle size increase of small particles would be more evident and this change may be due to coalescence or flocculation of the particles, and/or reaction of water with isocyanate which produces urea.

Dn of the water/isocyanate system increased slightly over the first two hours of induction time and then more significantly between two and six hours . The number distribution curve initially had a narrow single peak at ~60 nm, which is indicative of the main particle population at induction times of less than two hours. At two hours, most of this population remains but a smaller population at ~200 nm became evident. By four hours, the two populations had begun to merge as evidenced by a significant broadening of the higher portion of the curve up to 240 nm. At the four-hour time, it was also noticed that the temperature of the vial containing the admixed coating had increased significantly, indicating that the exothermic isocyanate-water reaction was proceeding significantly. This was examined further in calorimetry work as discussed in the following.

The PUD-1/isocyanate dispersion had a bimodal distribution with the main particle population at 60 nm and a much smaller population between 200 and 600 nm. This is consistent with results reported by Kubitza[13] but considerably smaller than that reported by Jacobs and Yu.[4] The smaller particles may be from the PUD-1 dispersion; however, our results with PUD-1 and previous reports[4] indicate this dispersion has a particle size much smaller than 60 nm. Based on the particle size results reported, these smaller particles most likely are from the isocyanate dispersion. The larger particles (200-600 nm) in the PUD-1/isocyanate dispersion are certainly isocyanate. Contrary to previous reports,[4,13] the distribution did not change much over the five-hour induction period. Dn did not change and Dw decreased only slightly from 323 to 261 nm. From these data, it does not appear that coalescence is occurring to a major extent.

The ACPU-1/isocyanate dispersion had a slightly different particle size distribution than the water/isocyanate and the PUD-1/isocyanate dispersions. There was a large population between 50 and 80 nm which is indicative of the ACPU-1 particles and probably some isocyanate particles. A second, much smaller population existed in the 100 to 200 nm range, also from isocyanate. Over the five-hour induction period, Dn increased only slightly from 66 to 81, and Dw decreased from 206 to 148 nm. Initially, Dw/Dn was 3.1 but by two hours it had decreased to approximately two, after which it was constant over the remaining induction period. In comparing the ACPU-1 results with those of the PUD-1, both had a main distribution in the 60 to 80 nm range which remained relatively constant over the five-hour induction time. Both dispersions with the isocyanate had a smaller population at larger diameters; however, this population was in the 100 to 200 nm range with ACPU-1 and 200 to 600 with PUD-1. For both systems, the smaller particles remain relatively constant over the induction time while the larger particles appear to decrease slightly in size.

The particle size results illustrate that there is a significant difference in isocyanate particle size depending on the component in which it is dispersed. It appears that the ACPU-1 emulsifies the isocyanate into smaller particles than in the other systems evaluated. This would tend to improve film formation since smaller particles coalesce more completely. In addition, the results show that particle size of the isocyanate/polymer dispersions does not change significantly over time in the admixed state during typical induction times. This suggests that particle coalescence or flocculation does not occur to a significant extent.

Isocyanate Reaction in the Admixed State

Isothermal (21°C) calorimetry experiments as a function of induction time were performed on reaction mixtures to identify timescales for the reaction chemistry in the system. *Figure* 5 illustrates the response for three systems: (a) water/isocyanate; (b) ACPU-1/isocyanate; and (c) PUD-1/isocyanate. In all three, the point of mixing is observed as an initial sharp exothermic rise in heat flow. This is almost certainly caused by a heat of mixing which lasts over the first 15 to 20 min of induction time.

The water/isocyanate system displays several exotherms which follow the heat of mixing. The first occurs approximately 2.6 hr after mixing, a second is at 4.8 hr, and a broad exotherm is observed between 8.2 and 11.8 hr. The exotherm at 4.8 hr correlates with the temperature rise observed during in-situ particle size measurements of this system. It is interesting to note that Dn for this system increased significantly between two and six hours, which coincides with the first two exotherms. During the reaction time urea formation is certainly occurring. Although it is not entirely clear what intermediate chemical reactions are responsible for each of the exotherms observed, various experimental results provide some evidence. As *Figure* 1 illustrates, the reaction of isocyanate with water to form urea consists of several steps. In the first step, carbamic acid is produced which subsequently decomposes into amine and carbon dioxide. The reaction sequence continues with amine and remaining isocyanate to form urea. During viscosity/pot life studies, a substantial increase in foaming was observed five to six hours after mixing the two components. This suggests that the first exotherm may be due to production of carbarmic acid, while the second exotherm is due to its decomposition which produces carbon dioxide. In addition to these reactions, isocyanates also can react with previously formed urethanes and ureas to form allophonates and biurets. It is believed that these play only a minor role in the film formation of 2K waterborne polyurethanes but they may be responsible for some of the latter exotherms in *Figure* 5a.

The ACPU-1 system (b) exhibits an exotherm which continues from the heat of mixing and reaches a maximum exothermic heat flow approximately five hours after mixing. After this time, the heat flow decreases and essentially returns to the baseline by ~8 hr. The PUD-1 exotherm reaches its peak approximately 2.2 hr after mixing. It is not as intense but it is broader (in time) than that with the ACPU-1.

It would seem highly desirable to apply these coatings between the time of mixing and not long after the maximum heat flow. If applied after this time, molecular weight and crosslinking buildup may prevent complete particle coalescence after application.

Concerning the relative rates of the curing reactions in these systems (i.e., hydroxyl-isocyanate and water-isocyanate), the calorimetry data strongly suggest that the reaction of isocyanate with hydroxyl groups begins almost immediately, while that with water is delayed for more than two hours. This is in agreement with previous reports.[4,15,16] Pertaining to application and cure of these systems as coatings, it certainly is desirable for curing reactions to occur quickly for drying and establishment of properties. However, pot life is also a consideration, and if reactions occur too quickly, pot life may be undesirably short. This issue is addressed in the following.

Pot life of the ACPU-1 coating was evaluated by performing viscosity measurements (Zahn 2 cup) as a function of

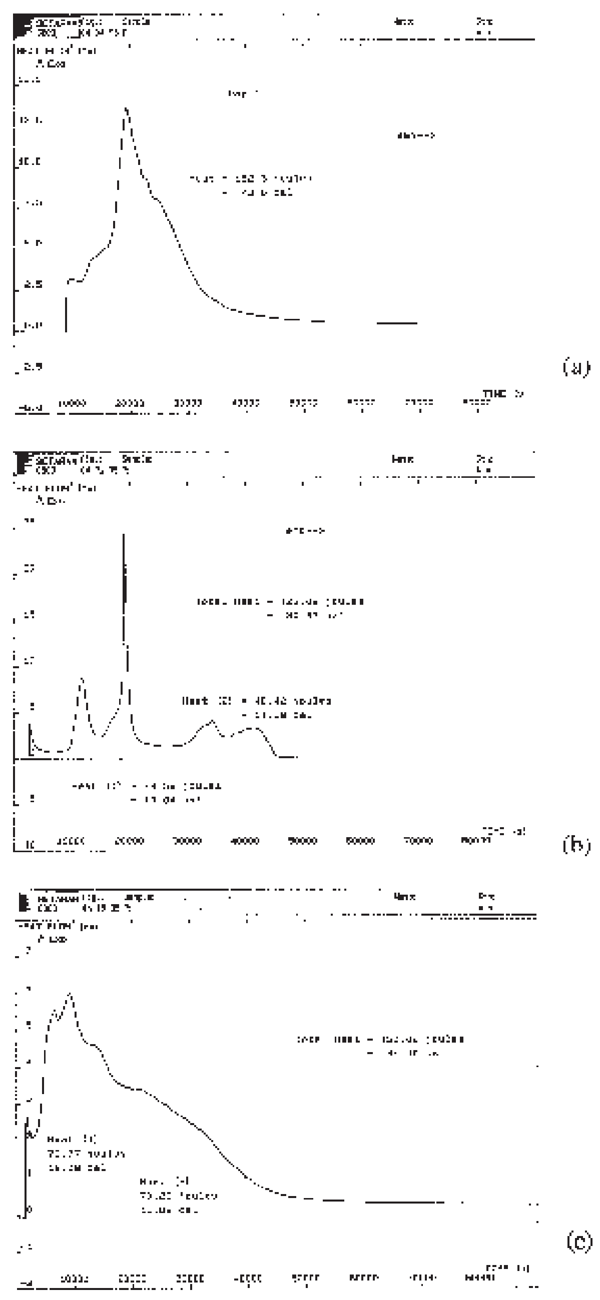

Figure 5—Calorimetry results for (a) water/isocyanate, (b) ACPU-1/isocyanate, and (c) PUD-1/isocyanate.

Table 6—Catalyst Level Effect on Zahn 2 Cup Viscosity (sec) versus Induction Time

	Catalyst Level (%)							
Induction Time (hr)	0	0.02	0.03	0.04	0.05	0.06	0.08	0.1
0.25	22.2	23.2	23.1	23.8	24.5	24.5	25.3	25.7
0.5	22.1	23.5	24	24.5	25.2	26.4	26.7	27.9
1	22.2	24.9	25.7	27	28.8	28.1	29.2	29.8
1.5	22.7	26.4	26.9	28.5	30	29.3	28.8[a]	26.5[a]
2	23.9	27	27	27.7[a]	26.9[a]	24.2[a]	24.4	25
3	25.2	27.3	27.1	26.6	25.5	26	28.1	29.8
4	25.3	25.7[a]	26.7[a]	25	28	—[b]	—[b]	—[b]
5	26	26	25	—[b]	—[b]			
7	26	—[b]	—[b]					

(a) The admixed coating had become slightly foamy.
(b) The admixed coating had become extremely foamy.

induction time. In these experiments, catalyst level was varied from 0 to 0.10% based on polymer solids. These admixed coatings initially had a viscosity of ~35 sec. Approximately six percent deionized water was added to reduce the viscosity to the 22 to 26 sec range. As can be seen in *Table* 6, the viscosity of the coatings with catalyst increased slightly over the first one to two hours, after which viscosity decreased slightly. As the viscosity decrease occurred, the coatings appeared to become slightly foamy but application at this time still yielded coatings with good optical, chemical, and mechanical properties. It is suspected that the viscosity decrease and observed foam is caused by generation of CO_2 from the isocyanate/water reaction. The amount of foam increased over time until the system was excessively foamy. Others have reported similar observations.[1,6] These results are quite different from those of traditional 2K solvent-based polyurethane systems which increase in viscosity as the molecular weight and crosslinking build until the system eventually gels. In the case of these 2K waterborne polyurethanes, the pot life appears to be limited not by viscosity/gelling effects, but by generation of carbon dioxide and the resulting foam. The use of optimum catalyst level, defoamers, and agitation rate may be used to control this effect and extend pot life considerably.

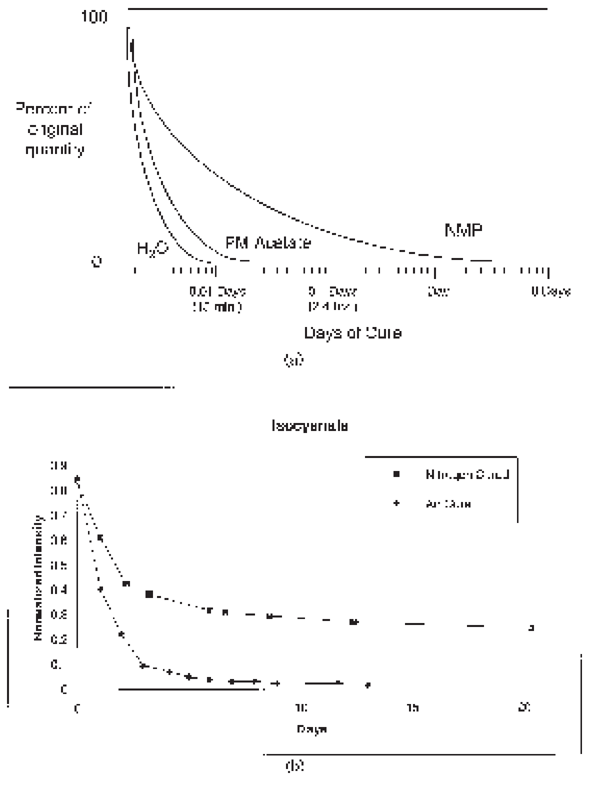

Figure 6—Plot of (a) disappearance of water, PM acetate, and NMP in curing coating; and (b) disappearance of isocyanate peak intensity with and without moisture during cure as monitored by IR as a function of time.

It is interesting to note with the 0.04% catalyst system (*Table* 6) that the initial observation of foam after two hours and excessive foam at five hours coincides with the reaction times observed from the calorimetry study with this system which reached a peak heat flow at approximately five hours.

Evaporation of Volatiles and Particle Coalescence after Application

After application, the volatiles within the coating begin to evaporate, causing the particles to come closer together until they come into contact with each other "throughout the film." This marks a critical solids concentration and point in time during the film formation process. When the particles come into contact, the potential for coalescence and reaction of isocyanate with hydroxyls increases dramatically. The solids content of the coating at this point (i.e., when particle to particle contact is first made throughout the coating) is equal to the packing factor of the dispersion particles. Many researchers have observed hexagonal close packing of dispersions with narrow particle size distributions.[9,22,23] In this case, the volume packing factor is 0.74. Others have observed a random close-packed arrangement[24] in which case the packing factor can be determined by applying the dispersion particle size distribution to an empirically derived algorithm.[25,26] Using this approach, the packing factors for the systems in this study are estimated as 0.68. This indicates that the critical solids volume concentration during drying, which causes particle to particle contact throughout the coating, is between 68 and 74%. With the density of the polymer and volatile constituents estimated at 1.15 and 1 g/ml, respectively, this critical concentration is 71 to 77% by weight.

During in-situ Raman and EIS analysis of applied coatings, distinct changes in the response spectra were observed between 15 and 30 min. Results indicated that the coatings appeared to change from a fluid state to a thinner, solid-like state as would be expected during drying. Subsequent weight loss versus time data (*Table* 7 and *Figure* 6) indicated that by 15 min after application, the ACPU-1 coating was above this critical solids concentration. Other weight loss studies on this system were conducted with VOCs ranging from 150 to 350 g/L and catalyst concentrations up to 0.10% (which encompasses the typical range for these formulation parameters). All of these systems reached this critical solids concentration within 15 min as well. These results directly indicate that within this 15 min time frame after application, particle-to-particle contact is completed throughout the coating. As a consequence, particle coalescence within the film should be occurring relatively rapidly. However, it must be noted that if induction times were substantially extended hours into the pot life (i.e., well past exotherms), the urethane and urea forming reactions would build molecular weight and crosslinking to the extent that diffusion of the co-reactants may be limited and even close packing of the particles may not allow coalescence to occur.

IR spectroscopy was used to track the evaporation of water and organic solvent components of the coating system after application. Water was tracked by following the 3384 cm^{-1} band, propylene glycol methyl ether acetate was tracked using the 1236 cm^{-1} band, and N-methylpyrrolidone (NMP) was studied by following the 1296 cm^{-1} band over time. Decreases in concentrations (from peak intensity decreases versus initial values) are plotted for these three components of the curing coating in contact with laboratory atmosphere (*Figure* 6a). Water and PM acetate were decreased to trace levels within 15-30 min after application, while NMP dropped to trace levels within about six hours.

The rapid evaporation of water correlated well with weight loss results described, as was the relatively rapid evaporation of PM acetate. The vapor pressures of water and PM acetate are 18.65 and 3.8 torr (at 21 and 25°C, respectively). The vapor pressure of NMP is lower (0.29 torr at 20°C), and the evaporation time for NMP was much longer. However, it was in marked contrast to conventional expectation that NMP remains in the coating until much later in cure, and was much shorter than predicted by vapor pressure arguments. The effect of NMP on film formation and development of mechanical properties in the film must be considered. It should be noted that although these IR studies showed volatile loss within six hours, trace levels of water and solvents may remain in the film for days or possibly weeks.

Isocyanate Reaction after Application

The reaction of isocyanate with hydroxyl groups and water within the dispersion was monitored with IR-ATR spectroscopy. These experiments were done with specimens at ambient conditions as well as with a dry nitrogen purge. *Figure* 6b illustrates the isocyanate intensity loss over time after coating application. From this data it is obvious that the coating in ambient conditions is curing relatively rapidly, with over 75% of the isocyanate reacted within the first two days and over 90% after three days. This suggests that substantial crosslinking has occurred within this time frame, further suggesting that chemical resistance and mechanical integrity of the film is also improving. As will be further illustrated and discussed, this agrees well with coating characterization results. By seven days after application, 97% of the isocyanate has reacted and it appears virtually complete by 13 days. Due to the high NCO/OH ratio some of this reaction is most certainly due to moisture cure of the isocyanate to form urea.

Figure 6b also illustrates a stark difference in the curing of the coating in ambient laboratory conditions versus a dry nitrogen atmosphere. It should be noted that these systems were formulated at an NCO/OH ratio of 2.0 in order to allow for reaction of isocyanate with water. Although the weight loss and Raman data presented indicates quick evaporation of the water, the IR results clearly indicate moisture curing of the systems still occurs with trace amounts of water remaining from the dispersion and/or moisture from the air. Furthermore, the ambient cured system is observed to cure at a much faster rate than that in dry nitrogen. Presumably, this would indicate quicker property development of the coating as well. After cure at ambient conditions, XPS results after one week showed only traces of isocyanate functional groups in the C(1s) spectra, indicating that complete reaction had occurred in ambient cured coatings. XPS composition also showed a relatively high nitrogen/carbon ratio which reflects a significant ratio of urea/urethane in the cured coating.

Development of Film Integrity

A probe for the initial development of film integrity was EIS measurements made as a function of cure time. EIS spectra showed essentially gel behavior at early times (~15 min), however, by three hours after application, the spectra took on a film-like character. Equivalent circuit modeling of the three-hour point showed that pore resistance of the coating had climbed to 1 megaohm after 15 min immersion in electrolyte. This reflects the development of significant barrier properties in the curing coating, which are reflected in the increasing barrier to ionic penetration of the polymer system. After six hours, the coating barrier properties had achieved a maximum film character in the 15 min immersion experiments, stabilizing at a pore resistance of over 1 gigaohm. For example, after full cure, these coatings had a pore resistance of over 1 gigaohm after 15 min equilibration in electrolyte, and about 30 megaohms after 24 hr in electrolyte solution. EIS results showed that film formation had occurred to a significant extent by three hours after application, and that between

Table 7—ACPU-1/Isocyanate Coating Weight Loss and Solids Content After Application

Time After Application, hr	Coating Remaining, %[a]	Solids Content, %[b]
0	100	50
0.25	58	86
0.5	56	89
1	54	91
2	53	93
3	52	96
4	51	97
5	51	98
6	50	99
24	50	99
48	50	100

(a) Weight percent of coating remaining compared to weight at application.
(b) Weight percent of remaining coating present as solids.
Note: Theoretical solids content of the admixed coating is approximately 49.7% by weight.

Table 8—ACPU-1/Isocyanate Property Development

Day	Persoz Hardness (sec)	Solvent Resistance	Scrape Adhesion (kg)	Dry Tape (5A- No Removal)	Water Immersion
1	16	Fair	8	5A	No effect
2	32	Fair	8	5A	
3	50	Good	10	5A	No effect
5	55	Good	10	5A	No effect
7	59	Good	10	5A	
10	55	Good	10	5A	No effect
17	70	Good	10	5A	No effect

three and six hours after application, the film rapidly developed further barrier properties.

The development of coating mechanical properties and chemical resistance was monitored by evaluating adhesion, hardness, water, and solvent resistance up to 17 days after application (*Table* 8). The results indicate that water resistance and dry tape adhesion developed rapidly, as evidenced by acceptable performance 24 hr after application. The coating hardness developed at a slightly slower rate. The Persoz (pendulum) hardness improved quickly over the first three days and then gradually increased to a maximum at about 17 days. (Films which have cured for several months have values of approximately 70 sec.) Hardness development over the first three days is also evidenced by the scrape adhesion results in which the mode of failure at days one and two was indicative of a marring of the coating. Finally, solvent resistance tests were performed by double rubs of methyl ethyl ketone (MEK), toluene, and isopropanol, respectively. The coating response to these solvents during days one and two was marring of the surface and softening of the film. After that time, the coating resisted in excess of 200 double rubs with no effect. These results correlate well with the results from IR spectroscopy. By the third day, over 90% of the isocyanate has reacted (under ambient conditions). This indicates quite substantial crosslinking which would result in improved solvent resistance. In order to further substantiate these results, dynamic mechanical analysis of films during cure is currently being undertaken. These data will provide a direct indication of the rate of crosslinking within the polyurethane system after application.

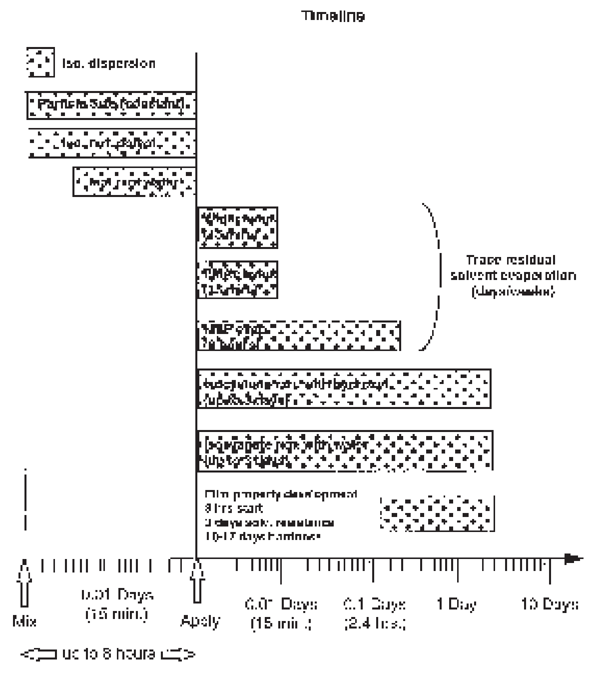

Figure 7—Timeline of events in film formation mechanism of 2K waterborne polyurethane coatings.

Property development of the PUD-1 system was reported by Jacobs and Yu.[4] They reported maximum solvent resistance, impact and hardness after two days, ultimate tensile strength after four to five days, storage modulus stabilization after two days, and tan delta stabilization after three days. These results would seem to be in general agreement with our findings for the ACPU system.

SUMMARY

In this work, a model for the mechanism of film formation for 2K polyurethane coating systems was proposed in terms of a timeline of interrelated events. A range of analytical methods were used to probe the relative times for the mechanistic events, and an overall framework for film formation was described. The specific events and their timeframes are shown schematically in *Figure* 7. The dispersion of isocyanate in the aqueous system appears to occur immediately upon addition and mixing. Particle coalescence during the admixed state was found to be minimal by particle size experiments. Isocyanate reaction with hydroxyl groups occurred within two to five hours, as evidenced by the maximum exotherm from calorimetry data. Reaction with water occurred at a much slower rate, as shown in calorimetry work on a water/isocyanate system. These results correlated well with pot life studies and CO_2 generation from the isocyanate/water reaction.

After application, evaporation of volatiles occurred within 30 min. During this time, a critical solids content of the coating was reached, such that particle-to-particle contact was completed throughout the film. When this occurs, diffusion of polymer molecules across particle boundaries leads to particle coalescence. This also favors the isocyanate/hydroxyl group reaction. Isocyanate reactions after application are 80% complete within three days, suggesting substantial crosslinking by this time. To account for isocyanate/water reaction and ensure complete hydroxyl reaction, NCO/OH ratios were 2.0. Studies on film property development illustrated that barrier properties began to be established within three hours, and chemical resistance developed within three days.

This study was completed with a limited set of formulation and application parameters. It did not fully evaluate the effects of level of agitation, solvent concentration, catalyst concentration, induction time, temperature, and humidity on resulting film formation. Further work to probe these variables and their effects on cure and coatings properties is in progress. This is the first detailed examination of film formation for this class of polyurethane coatings and provides a framework for further study and for improved understanding of this growing coating technology.

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